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THE STUDY OF CHARGE CARRIER TRANSPORT ON THE CALAMITIC LIQUID CRYSTALS “ 5, 5’-DI-(ALKYL-PYRIDIN-YL) - 2’ BITHIOPHENES”

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Abstract

The hole and electron mobilities in both types of calamitic liquid crystals **C9** [5,5’-Di-(5-n-nonyl-pyridin-2-yl)-2,2’-bithiophenes] and **C10** [5,5’-Di-(5-n-decyl-pyridin-2-yl)-2,2’-bithiophenes] were studied. The charge carrier mobilities were strongly electric field dependent. The mobilities decreased continuously with increase in the electric field up to a certain value, after which it became constant. Both types of charge carrier mobilities are independent of the temperature over our temperature range. The qualitative feature of our results could be tentatively explained by the Monte–Carlo modeling proposed by H Bassler. However, the results require further study for better understanding.

Introduction

Why organic semiconductors ? (comparing with Si or Ge)

- Often easier to purify
- Good solubility in organic solvents
- Low temperature processing
- The mobility is comparable to amorphous silicon thin films
- Enable one to fabricate uniform large-area thin films
- Compatible with flexible substrates

Parameters effecting mobility

- Aromaticity
- Closely packed molecular alignment
- Large overlap or transfer integral
- High positional and rotational order

Liquid crystals containing pyridine and thiophene molecules

Liquid crystals containing pyridine show complex mesomorphic behavior. Higher ordered mesophases like SmG and SmH are often observed in pyridine containing liquid crystal near room temperature [1] .

Similarly, the presence of highly polarizable sulfur atoms increases the transfer integral of thiophene molecules due to a large van der Waal's radius. Then, the participation of the lone electron pairs on sulfur in the delocalized π-electron system plays an important role in the charge carrier transport phenomenon and in close molecular packing in the thiophene molecules[2,3].

These facts make pyridine and thiophene based liquid crystals attractive candidates for the study of their charge carrier mobility and applications in electronic devices.

Molecular structure and phase diagram of the experimental materials

The materials used in our experiment are **C9** [5,5’-Di-(5-*n*-nonyl-pyridin-2-yl)-2,2’-bithiophenes] and **C10** [5,5’-Di-(5-*n*-decyl-pyridin-2-yl)-2,2’-bithiophenes][4]. The molecular structure of the experimental materials is shown in Figure 1. The molecule consists of a core unit of two thiophene and two pyridine units.

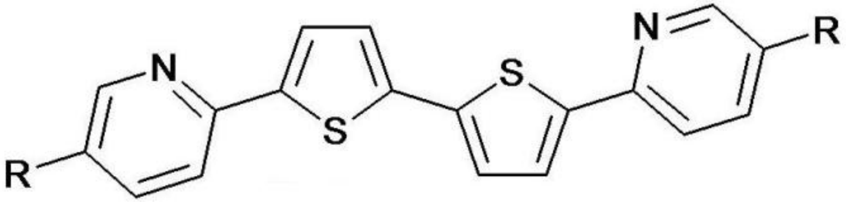
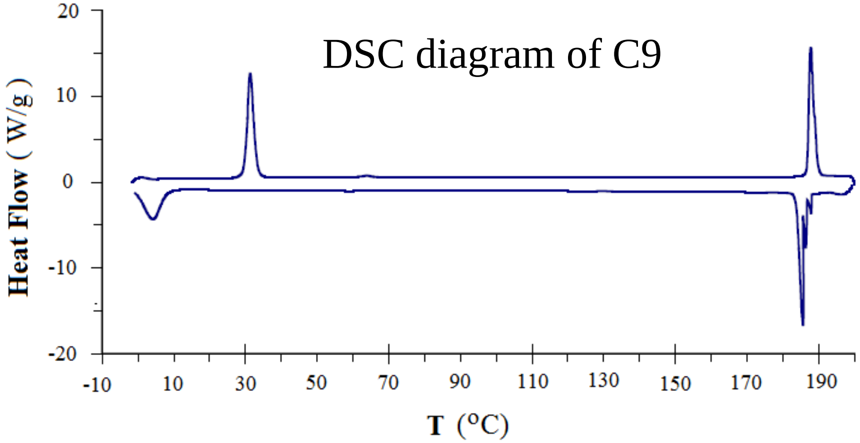
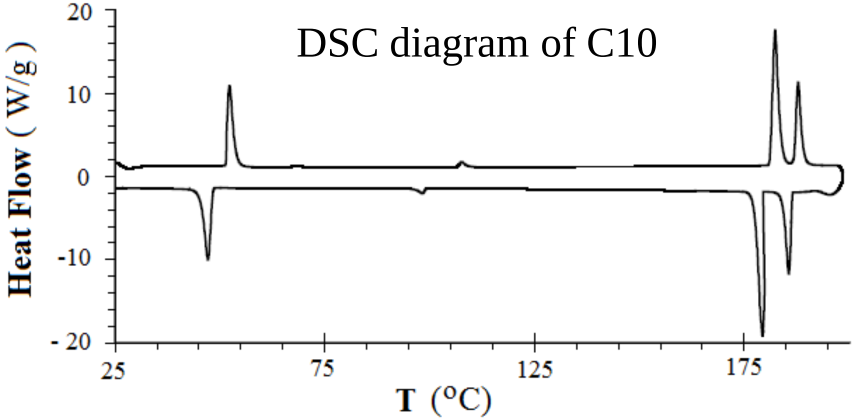


Figure 1**:** Molecular structure of C10 (R= $C_{10}H_{21}$) and C9 (R= C_9H_{19}).

Phase Transition Temperatures of C9 and C10





C9 → K [4.2] Sm1 [59.7] *SmG/K1* [185.1] SmC [187.1] N [188.3] Isotropic
C10 → K [48.5] Sm1 [96.1] *SmG/K1* [179.0] SmC [186.7] Isotropic

Experimental Set Up

The charge carrier mobility of the materials was measured by the time of flight (TOF) method as shown in figure 2. The experimental set up is shown in figure 3.

Working Formula :

$$\mu = \frac{\upsilon}{E} = \frac{d^2}{V\tau}$$

μ= Charge carrier mobility
d= Thickness of the sample
E= Electric field across the sample
τ =Time of flight

Limitation:

At lower temperature, low voltage gave dispersive traces, which made it difficult to locate the transient time for the TOF in the trace. At higher temperature, high voltage produced space charge.

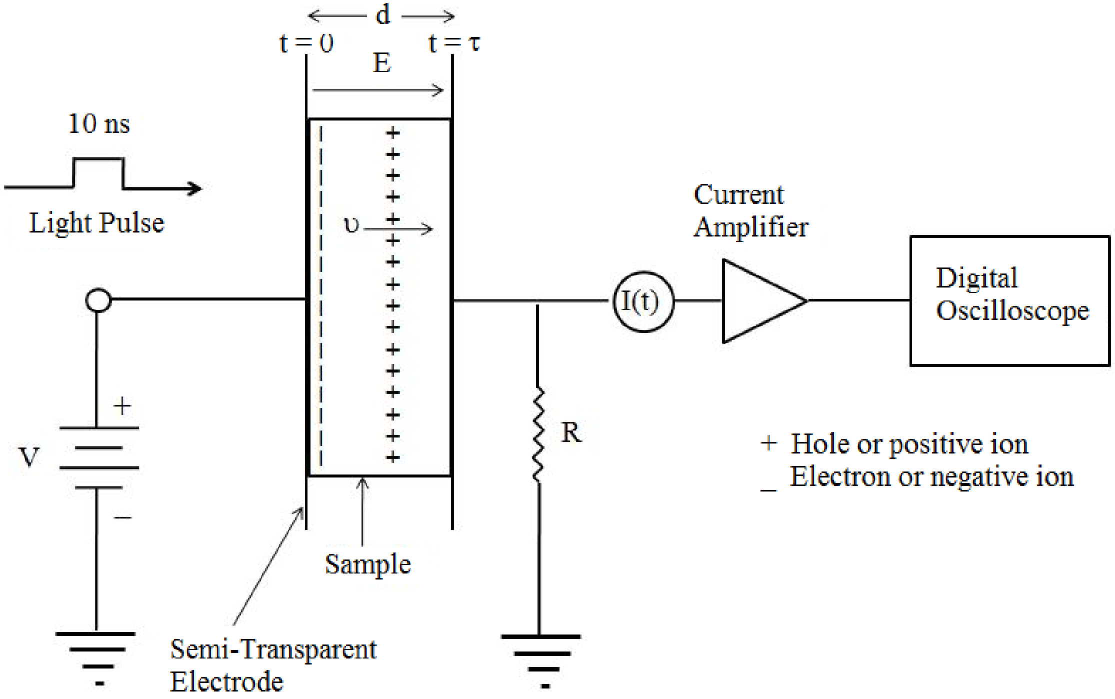


Figure 2 : Basic set up of the time of flight experiment

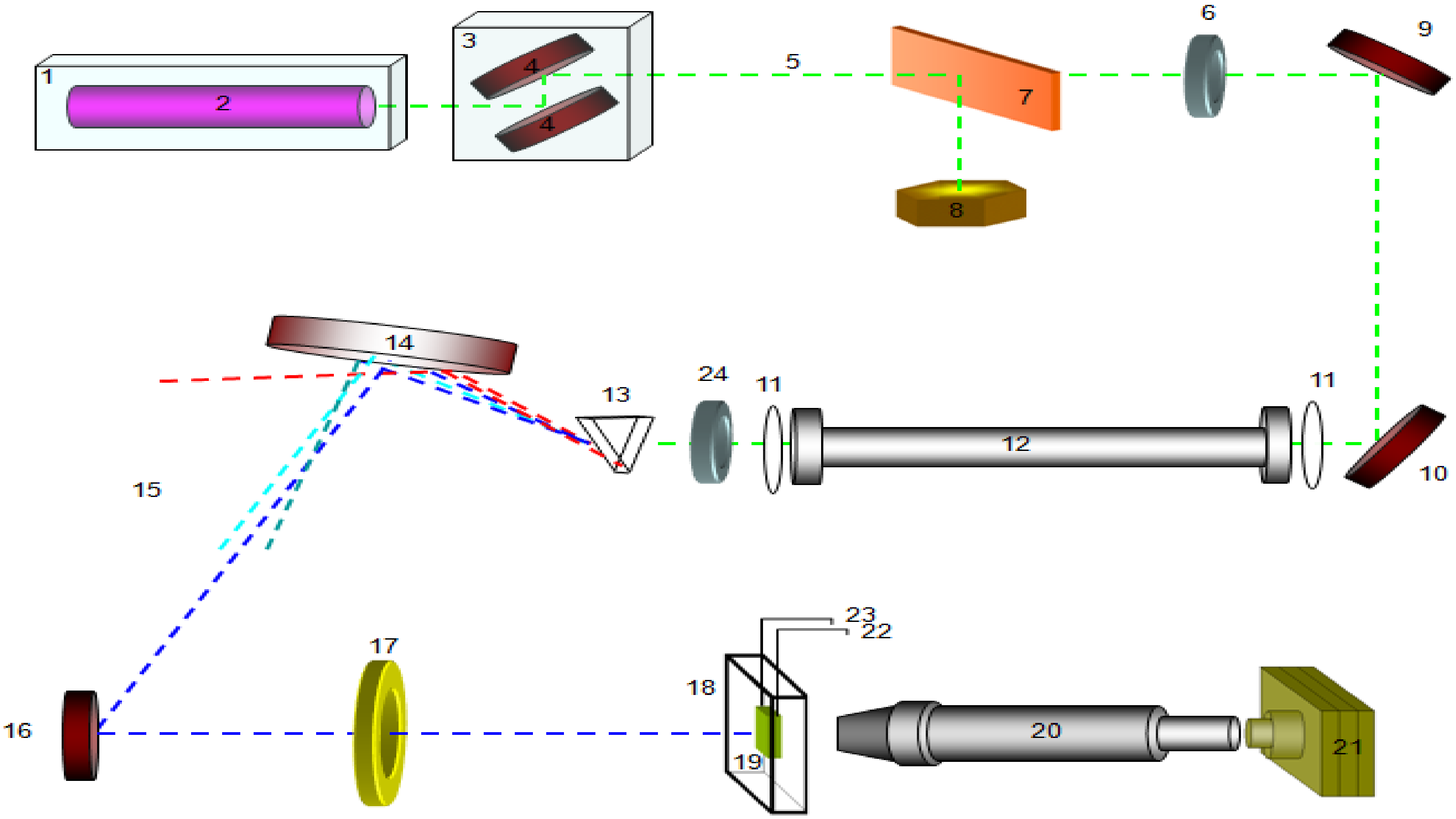


Figure 2: Experimental Set Up

(1)10 ns/0.7 J Surelite Nd:YAG Laser (2)Laser rod (3)SSP-Surelite Separation Package box (4)Dichroic mirrors (5)Pure Harmonic Light after reflection from Dichroic mirrors (6)Half wave plate (7)Glass slide (8)Fast trigger detector (9)Reflector (10)Reflector (11)Lens (12)Stimulated Raman Shifter (13)Prism (14)Mirror (15)Light of desired wavelength (16)Mirror (17)Polarizer (18)Hot stage (19)Sample (20)Polarizing microscope (21)Camera (22)Voltage connecting wire (23)Signal connecting wire (24)The beam collimator.

Results

The hole and electron mobilities versus temperature for C10 at an electric field of 3 x 10^4 V/cm.

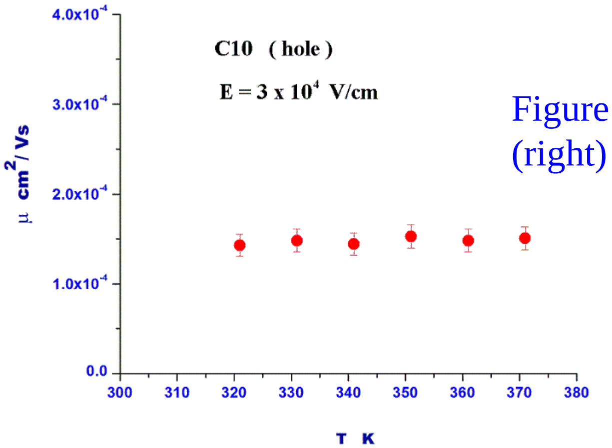
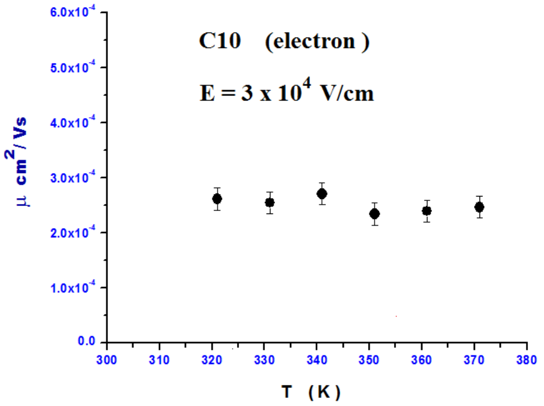


Figure 3 : The hole (left) and electron (right) mobility vs. temperature for C10



The hole and electron mobilities versus electric field for C10 at a temperature of 341 K

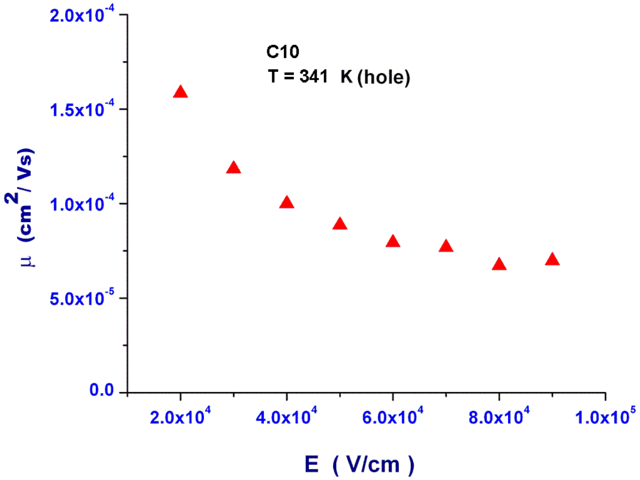
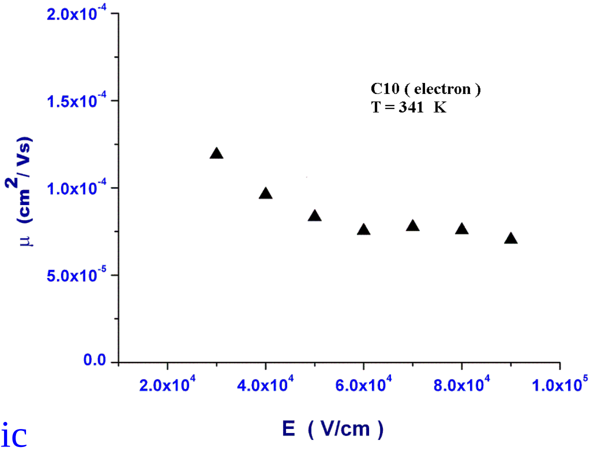


Figure 4 : The hole (left) and electron (right) mobility vs. electric field for C10 at 341 K.



The hole and electron mobilities versus electric field for C9 at a temperature of 341 K

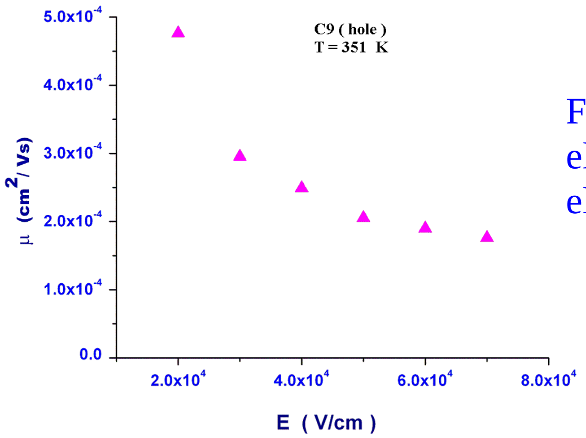
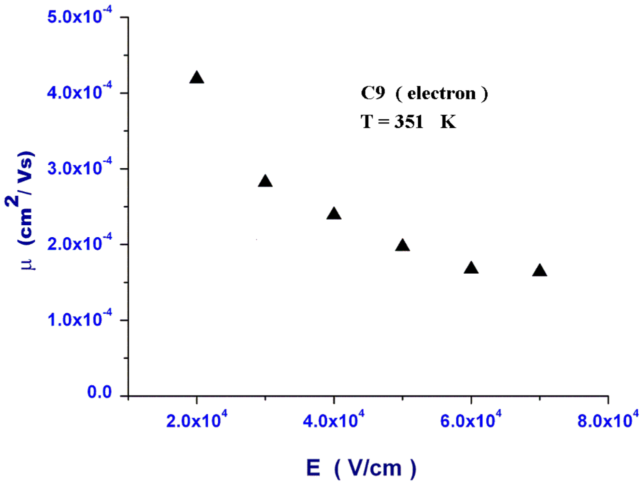


Figure 5 : The hole (left) and electron (right) mobilities vs. electric field for C9 at 351 K.



The hole and electron mobilities versus temperature for C9 at an electric field of 5 x 10^4 V/cm

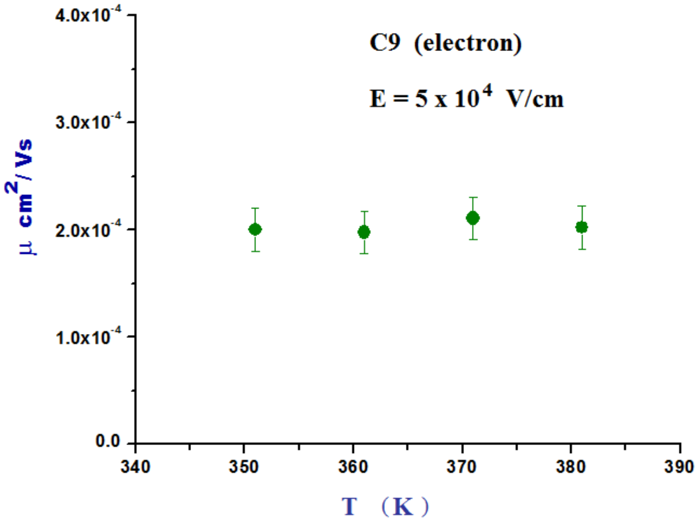


Figure 6 : The electron mobility vs. temperature for C9 at 5 x 10^4 V/m .

Discussions

- In our results, the charger carrier mobilities are not affected significantly by the change in temperature for both C10 and C9 over our temperature range. This argues against transport due to ions.
- Our observations also showed that hole and electron mobilities were strongly electric field dependent in both compounds C10 and C9. The mobility decreased continuously with increasing electric field up to 6 x 10^4 V/cm after which it became almost independent of the electric field.

- Qualitatively, a similar type of electric field dependent mobilities have been observed in TAPC doped BPPC at 329 K[5] and poly(3-hexylthiophene) at 310 K[6]. However, the mobilities of BPPC and poly(3-hexylthiophene) depend on the temperature as well.

- There are at least three theories of hopping conduction that might be applicable to these materials. Central to all of the theories is the basic picture of the hopping rate between two sites being proportional to the product of a transfer integral (J) depending on the overlap of , e.g., HOMO orbitals for hole transport, and a Boltzmann-like factor involving $\Delta\varepsilon$, the difference in site energies.

- Firstly, the model of Emin[7], based on the pioneering work of Holstein[8], considers carriers in an ordered system. Here the field dependence can arise due to the carrier's need to absorb/emit phonons as they jump from a site and relax from their field-accelerated states to a new site. A larger field thus leads to a greater number of carrier-phonon vertices and therefore strongly decreased mobility. Indeed, in many cases, $\mu \sim \exp[-E^2] \rightarrow 0$ as $E \rightarrow \infty$.

- Other theories include the effects of various sorts of disorder on the hopping. Energetic (diagonal) disorder, characterized by a width σ, arises when there is dispersion in the energy of hopping sites. Positional (off diagonal) disorder, represented by Σ, arises either when sites are not equidistant or the molecular orientations (e.g., the relative orientation of the molecules' π-orbitals) on the sites are different. One such theory assumes spatially uncorrelated Gaussian-distributed disorder[9] while the other invokes spatially correlated disorder arising from the comparatively long-range fields of random dipoles. We will find it sufficient to discuss the former, in the context of which we describe the experimental consequences of different combinations of σ and Σ[9] .

- Consider first the case of small σ and Σ. In this case the integral J is constant and each site offers almost the same energy to the carrier. Therefore, the hopping rate is field independent and the mobility $\mu \sim R/E \sim 1/E \rightarrow 0$ for large E.

- In the case of $\sigma \neq 0$, $\Sigma = 0$, i.e., pure diagonal disorder, the application of an electric field tilts the free-energy surface, reducing the activation energy required to hop. With increasing E, the inter-site jump rate increases and so does μ. Both of these cases do not agree with the data.

- A more interesting situation manifests when $\Sigma \neq 0$. Here, there exist sites that act as traps ("dead ends") where there is insufficient overlap ($J \sim 0$) to easily pass to another site. When E is small this is not a problem-the charge can simply hop " backwards " to a previous site. However, as E increases a backwards hop involves a Boltzmann factor $\exp[-eEa/kT]$ (a is the hopping distance) and the mobility therefore falls with E. If the energetic disorder is also substantial, the simulations of Bassler[9] find that the aforementioned reduction in the activation energy overcomes the effects of "dead-ends" at sufficiently large fields and the mobility rises, i.e., μ is non-monotonic (or at lease almost flat for large fields). As seen in figures 4 and 5, our measured mobility as a function of field reaches a "plateau" at around $E \sim 10^5$ V/cm, consistent with the beginning of a reversal in sign of $d\mu/dE$.

- Some caveats are in order. Firstly, the TOF current transients were quite dispersive, though they generally retained clear changes in slope that we identified with TOF. As has been discussed in ref.[10], Scott et. al., this definition of the TOF in dispersive media can be highly deceptive, with the “real” TOF being substantially larger than one obtained using our procedure. To this end, we have tried the semi-phenomenological approach of ref.[10]. Unfortunately, our data do not appear to conform to the functional form proposed in this reference. A better approach would be the Monte – Carlo modeling of ref [9]. We note, however, that we believe that the qualitative features discussed here (decreasing μ with E, a plateau at high E, and little T dependence) will probably remain regardless of the definition of the TOF.

- Secondly, the application of Bassler’s model raises a number of difficult questions.

- (i) The theory predicts a temperature dependence. We find an essentially temperature-independent mobility. While T-independent transport has been observed before, i.e., in hexaalkyloxytriphenylenes, it appears to be due to dynamic disorder[10], which is unlikely (though not impossible) in the present highly ordered systems.

- (ii) We note that the theory of ref.[9] indicates that, for the development of a plateau-like feature in μ(E), the normalized disorder parameter $\sigma' = \sigma/k_B T$ must be ~ 1.5 or greater. For our data at T=70 °C , this implies σ/k_B ~ 455 K which, in turn, implies that the mobility should be a increasing function of T in the experimental regime, $\mu \sim \exp[-2x10^5/T^2]$. This is not observed.

- (iii) Furthermore, the theory depends on substantial energetic and positional disorder. It is not clear how such disorder might arise in our samples.

- These issues require further study, the former via accessing larger regimes of T and E, and the latter by structural studies of the rather puzzling S_2 phase found in C9 and C10 at these temperatures.

- Pyridine moieties often induce very ordered smectic phases and therefore, one might expect, large mobilities. However, we found the mobilities of bis-alkylpyridinyl-2,2’-bithiophenes (C10 and C9) were of order 10^{-4} cm^2/Vs, which was an order of magnitude smaller than the mobility $10^{-3} cm^2/Vs$ of bis-alkylphenyl-2,2’-bithiophenes[11]. Hence, more theoretical work need to be done for better understanding of the roles of pyridine in determining mobility.

Conclusions

1. We studied the mobilities of both types of charge carriers i.e. electrons and holes in the smectic liquid crystals C9 [5,5’-Di-(5-*n*-nonyl-pyridin-2-yl)-2,2’-bithiophenes] and C10 [5,5’-Di-(5-*n*-decyl-pyridin-2-yl)-2,2’-bithiophenes].

2. Pyridines, though known to assist in the formation of high-order smectic phases, appear to lower mobility.

3. Both electron and hole mobilities were strongly electric field dependent in both materials. The mobility decreased continuously with increasing electric field up to a certain value, after which the mobility becomes constant.

4. Both types of charge carrier mobilities are independent or very weakly dependent on the temperature. We tentatively describe our data using Basseler’s Theory of disordered hopping conduction.

5. The mobility of C9 was greater than C10.

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